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"Conducting and Magnetic Polymers"

by

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Polymers that contain conjugated backbones are being prepared to be studied as materials which show interesting levels of conductivity, photoluminescence and ferromagnetism. The materials being prepared contain backbones that are polyacetylenes or in some cases alternating polyene-arene repeat units. When the arene units are coupled in the para position, materials with conductivity and luminescence properties are produced. When the arene units are metacoupled, materials which may show ferromagnetic properties are synthesized. Key to the study is the development of methods for the controlled synthesis of the materials and the development of design principles that guide the synthesis of materials with optimized properties.

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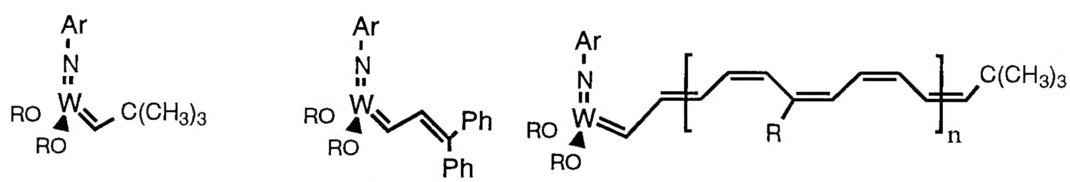
The objective, approach and scientific conclusions derived from the research effort.

Brief Description of Project.

Polymers that contain conjugated backbones are being prepared to be studied as materials which show interesting levels of conductivity, photoluminescence and ferromagnetism. The materials being prepared contain backbones that are polyacetylenes or in some cases alternating polyene-arene repeat units. When the arene units are coupled in the para position, materials with conductivity and luminescence properties are produced. When the arene units are metacoupled, materials which may show ferromagnetic properties are synthesized. Key to the study is the development of methods for the controlled synthesis of the materials and the development of design principles that guide the synthesis of materials with optimized properties.

Significant Results.

The last detailed study of the polymerization of substituted cyclooctatetraenes was completed and published during the last year. Since that time, the major emphasis has been on the development of methods for the controlled synthesis of segments of polyacetylene for use in block synthesis. Our original route to PA involved the use of catalyst **I** dissolved in the neat monomer. When we attempted to dilute the system and to prepare more controlled structures, it was observed that in noncoordinating solvents the growing chain underwent extensive backbiting reactions to give benzene or its derivatives. In coordinating solvents the growing chains were "living" but the initiation of the catalyst was very inefficient. Only a few percent of the catalyst initiated during the time or the reaction. This resulted in broad molecular weight distributions and the extremely inefficient formation of polymers with controlled segment lengths. Apparently in system **I** the alkyl substituted initiating carbene is much less active than the propagating end group of **III**.



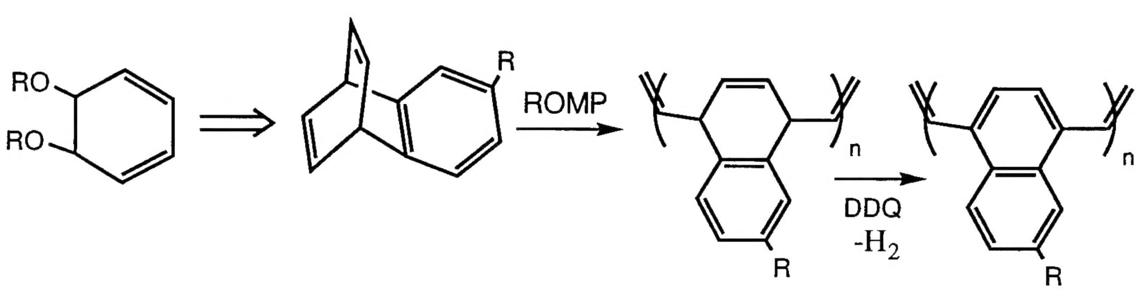
I initiating carbene **II** new initiating carbene **III** propagating carbene

From measurements of the ratio of initiating species to propagating chains in a reaction system, it can be estimated that the k_p/k_i is greater that 10^4. Consequently an attempt was made to design a system in which the initiation rate and propagation rate would be similar. To accomplish this the reactive propagating chain end must be similar to the initiation group. Consequently, complex **II** was used to polymerize COT derivatives.

During the last granting period we found that this catalyst efficiently initiated

the polymerization of substituted COTs. Polydispersities of 1.5 were obtained in these polymerizations. Additionally, we have found that the molecular weights of the polymers are directly dependent on the ratio of monomer to catalyst. Consequently, we can generate soluble polyacetylenes and vary the molecular weight distribution simply by changing this ratio. Under typical conditions, we have found that the ratio of the rates of initiation to propagation is equal to 1, which can be rationalized by the fact that the initiating carbene **II** (a conjugated vinyl alkylidene) resembles the propagating carbene **III**. At this stage of development an old problem returned to cause a major problem with this polymerization. We had found in the first studies of ROMP with tungsten catalysts that most polymerizations, even with highly strained monomers, formed a variable amount of a high molecular weight peak. This peak was variable and appeared to be connected to the source of the catalyst used. A similar observation was made with catalyst **II** when it was used to prepare polyacetylenes. An even more bothersome problem that is unique to polycot was the observation that a second component of the catalyst system also gave backbiting products. Consequently considerable effort has been put into the study of the mechanism of polymerization with these catalysts and in understanding the source of the second catalyst component. It is becoming apparent that these catalyst systems are much more complex that expected and that the activity of the catalyst is associated with impurities resulting from catalyst composition. We have now defined the factors and can now prepare well defined polymers now that the catalyst system is much better defined.

In addition to our work on PA, a new effort has been initiated into the development of ROMP routes to Polyphenylene Vinylene (PPV) and its derivatives. These routes are based on the availability of cyclohexadienediol for ICI. This material through Diels Alder routes can be converted into bicyclo[2.2.2]octadiene derivative that can be converted to prepolymers by ROMP. The route to polyparaphenylene has been completed and reported. A new route to polynaphthalenevinylene has been developed and has been used to prepare soluble vinylene naphthylene polymers.



The interesting feature of the naphthalenevinylene PNV route is the loss of H_2 instead of the larger fragments associated with the usual PPV routes. These soluble analogs have been demonstrated to be electroluminescent.

Significant advances in the preparation and characterization of organic polymers with novel magnetic properties were made. New polymers were prepared

that, on doping, produce a significant concentration of stable spins. Characterization by magnetometry (using SQUID) revealed significant ferromagnetic coupling throughout the material. These are the most substantial advances yet in the quest for a polaronic ferromagnet.

List of all undergraduate, graduate and post-doctoral associates funded through the grant.

Robert H. Grubbs

Graduate Students: Brenda Fiala, Christopher Gorman, Amy Pangborn, Michael Rock, Eric Ginsburg, Zhe Wu.

Post Doctoral Fellow: T. Randall Lee

Dennis A. Dougherty

Graduate Students: Kraig Anderson, Josh Jacobs, Tracey Burr.

Postdoctoral Fellow: Dave Shultz

List of all publications, presentations, patents and reports associates with the grant, and a list of transitions that resulted from your research under the ONR grant.

Robert H. Grubbs

ONR Publications.

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(227) "Poly-(1,4-Naphthalene Vinylenes): Synthesis of a New Class of Soluble Conducting Polymers. L. Pu, M. W. Wagaman, and R. H.Grubbs, *Macromolecules*, submitted.

Dennis A. Dougherty

53. A Theoretical Study of Bi(cyclobutadienyl) and Higher Homologues. Polycyclobutadiene as a Novel Organic Metal? J. Pranata, V. S. Marudarajan, and D. A. Dougherty, *J. Am. Chem. Soc.* **1989**, *111*, 2026-2030.

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66. Novel Magnetic Properties of a Doped Organic Polymer. A Possible Prototype for a Polaronic Ferromagnet. D. A. Kaisaki, W. Chang, D. A. Dougherty, *J. Am. Chem. Soc.*, **1991**, *113* 2764-2766.

67. Approaches to Magnetic Organic Materials. D. A. Dougherty, R.H. Grubbs, D. A. Kaisaki, W. Chang, S.J. Jacobs, D. A. Shultz, K.K. Anderson, R.Jain, P.T. Ho, E.G. Stewart, in *Magnetic Molecular Materials*, D. Gatteschi et al. Eds., Kluwer Academic Publishers: The Netherlands, pp. 105-120 (1991).

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80. Prototypes for the Polaronic Ferromagnet. Synthesis and Characterization of High Spin Organic Polymers. M. M. Murray, P. Kaszynski, D. A. Kaisaki, W. Chang, and D. A. Dougherty, *J. Am. Chem. Soc.* **1994**, *116*, 8152-8161.

Presentations.

1994 Karl Pfister Lecturer in Chemistry, Massachusetts Institute of Technology (RHG)

1994 Distinguished Syntex Lecturer, University of Colorado at Boulder (RHG)

1994 Frontiers in Advanced Materials, University of Illinois, Urbana-Champaign (DAD)

1994 Camille and Henry Dreyfus Lectures, Dartmouth College (RHG)

1995 Hutchinson Memorial Lectures, University of Rochester (RHG)

Awards.

1994 Fellow of the American Academy of Arts & Sciences (RHG)

1994 Fellow of the American Association for the Advancement of Science (DAD)

1995 ACS Award in Polymer Chemistry (Mobil Chemical Company) (RHG)

Highlight Three Publications

(1) "Thin Films of *n*-Si/Poly-$(CH_3)_3$Si-Cyclooctatetraene: Conducting-Polymer Solar Cells and Layered Structures." M.J. Sailor, E.J. Ginsburg, C.B. Gorman, A. Kumar, R.H. Grubbs, and N.S. Lewis, *Science* **1990**, *249*, 1146-1149.

This publication described the application of the polymerization techniques that had been developed to the fabrication of devices. This collaborative paper demonstrated that organic polymers showed considerable promise in the development of solar cells.

(2) "Voltammetric Characterization of Soluble Polyacetylene Derivatives Obtained from the Ring-Opening Metathesis Polymerization (ROMP) of Substituted Cyclooctatetraenes." T.H. Jozefiak, E.J. Ginsburg, C.B. Gorman, R.H. Grubbs, and N.S. Lewis, *J. Am. Chem. Soc.* **1993**, *115*, 4705-4713.

The fundamental electrochemistry of a family of polyacetylenes was demonstrated and the relation ship of the substitution pattern and the nature of the substituents of the redox properties. This information is essential for future uses of such materials in devices.

(3) "Soluble, Highly Conjugated Derivatives of Polyacetylene from the Ring-Opening Metathesis Polymerization of Monosubstituted Cyclooctatetraenes: Synthesis and the Relationship between Polymer Structure and Physical Properties." C. B. Gorman, E. J. Ginsburg, and R. H. Grubbs, *J. Am. Chem. Soc.* **1993**, *115*, 1397-1409.

This long paper described how the substituents of a conjugated polymer could be used to control the solubility properties and in turn the electrical and optical

properties. From calculations and the study of the absorption spectra of a family of polymers, the critical features that controlled and balanced the important physical and the electro-optical properties.

Presentation.

The 1994 Camille and Henry Dreyfus Lectures at Dartmouth College provided an opportunity to present a number of lectures to undergraduate and graduate students and to show how polymer research is part of organic/organometallic research.

Award.

The 1995-ACS Award in Polymer Chemistry (Mobil Chemical Company) was presented for the development of living organometallic catalysts and demonstrating their utility on the synthesis of a wide variety of polymers.

List of Transitions.

The polymers developed in the program were used to demonstrate the concept of a new type of polymer based sensor that could recognize and distinguish a number of vapors. The work was carried out in collaboration with Professor Nate Lewis for the JPL NASA lab in Pasadena.

Samples of the polymers were supplied to the Cavendish Laboratory to be used in their device applications.

The contacts developed through this grant resulted in a Collaboration with Robert F. Brady on the use of telechelic polyethylenes prepared by ROMP techniques for the preparation of non-stick coatings over a polyurethane base coat. Early results were promising. Further possibilities are being evaluated.